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[54] 发明名称 一种水泥促凝剂的制备方法及其应用

[57] 摘要

一种水泥促凝剂的制备方法，凡具有火山灰质活性的物质都可以作制备水泥促凝剂的基本材料，以基本材料 100 重量份为基准，加入  $\text{CaO}$  或  $\text{Ca}(\text{OH})_2$  10~50 份用水拌和经放置处理便能生成水化硅酸钙、水化铝酸钙等水化产物晶种，还可以用水泥熟料或水泥粉与水拌和后经放置处理便能生成水化产物晶种，作水泥促凝剂或者直接取代水泥混合材。本发明从根本上解决水泥缓凝的技术难题而且能最大限度地发挥掺氟硫矿化剂的作用，从而提高立窑水泥质量、降低生产成本。

# 权 利 要 求 书

1、一种水泥促凝剂的制备方法，其特征在于火山灰质材料粉磨后与氢氧化钙或氧化钙和水拌和经放置处理能够生成作水泥促凝剂用的水化硅酸钙、水化铝酸钙等水化产物晶种；凡具有火山灰质活性的物质都可以作为制备水泥促凝剂的基本材料，以基本材料100重量份为基准，按如下配方和工艺条件制备：

(1) 配方： $\text{CaO}$ 或 $\text{Ca(OH)}_2$  10~50份

$\text{NaCl}$ 或 $\text{CaCl}_2$  0~5份

$\text{Na}_2\text{SiO}_3$  0~10份

(2) 工艺条件：放置温度 室温~100℃

放置时间 7天~1天

2、一种水泥促凝剂的制备方法，其特征在于还可以用水泥熟料或水泥粉与水拌和后经放置处理能生成作水泥促凝剂用的水化产物晶种。

3、根据权利要求1所述的一种水泥促凝剂的制备方法，其特征在于火山灰质材料包括烧粘土或烧页岩或粉煤灰或油页岩渣或烧煤矸石或凝灰岩或氟磷炉渣或矿渣或火山灰。

4、一种水泥促凝剂的应用，其特征在于，按水泥100重量份为基准，用根据权利要求1、2、3所制备的水泥促凝剂取代水泥的2~15重量份，可用于加速水泥的凝结速度。

5、根据权利要求4所述的一种水泥促凝剂的应用，其特征在于该水泥促凝剂还可以直接取代水泥混合材。

# 说明书

## 一种水泥促凝剂的制备方法及其应用

本发明涉及水泥生产工业技术，是一种水泥促凝剂的制备方法及其应用。

国外自五十年代开始应用氟化钙作矿化剂烧制水泥的技术。该技术能改善水泥生料的易烧性、加速A矿（阿利特）生成并提高其水化活性，故已成为立窑水泥厂提高产质量、降低消耗的最有效途径之一。我国立窑水泥厂自八十年代初开始较广泛地应用氟硫复合矿化剂技术，已取得了较大的经济效益。但是，掺氟硫复合矿化剂烧制水泥，由于氟的作用， $Al_2O_3$ 大量固溶入A矿及铁相中去，使熟料中CA大量减少，阿利特水化时诱导期延长，所以常常使水泥的凝结时间延长，在实际应用中因水泥缓凝而影响了施工速度及工程质量。

为了解决水泥缓凝的问题，绝大部分厂家迫于无奈只能用降低氟化钙的掺入量来缓解缓凝的矛盾。但是氟化钙掺量不足，不但会大大减弱矿化剂的作用效果，而且还降低了A矿的活性，以致水泥强度大幅度下降。《水泥》杂志1994年第4期，第7~12页，题为“镇江水泥厂熟料慢凝原因分析及其对策”一文中公布了从配料和煅烧方面改善含氟硫水泥熟料慢凝的对策：控制 $F/SO_3$ 在0.42~0.55范围，创造条件掺加铝质校正原料，并在粉磨熟料时掺加5%市购早强型熟料，再采用快烧急冷制度，使熟料初凝时间可控制在3.5小时之内。它的不足之处在于不但改变了原有的生产工艺条件，要求配料和煅烧稳定，而且早强型熟料作外加剂成本太高。

如何能最大限度地发挥氟硫矿化剂的作用，又能控制好水泥的凝结时间，仍然是目前水泥厂家的一大技术难题。

本发明的目的在于克服背景技术的不足之处，研究出一种既能最大限度地发挥掺氟硫矿化剂的作用，又能控制好水泥凝结时间的水泥促凝剂。在磨制水泥时或使用水泥时，加入适量的水泥促凝剂，既能从根本上解决水泥缓凝的技术难题，使氟硫矿化剂技术进一步完善，又能提高立窑水泥质量降低生产成本。而对水泥性能没有产生任何不良影响。

本发明的目的可通过以下措施来达到：

本发明从研究掺氟硫矿化剂烧制的水泥缓凝机理出发，通过大量的实验及分析，找出具有火山灰质活性的物质作促凝剂的基本材料。它包括烧粘土或烧页岩或粉煤灰或油页岩渣或烧煤矸石或凝灰岩或沸腾炉渣或矿渣或火山灰，总之凡是与氢氧化钙或氧化钙和水拌和后经放置处理能够生成水化硅酸钙、水化铝酸钙等水化产物的

均可作为制备水泥促凝剂的基本材料，以基本材料100重量份为基准，按如下配方和工艺条件制备：

- (1) 配方： $\text{CaO}$ 或 $\text{Ca(OH)}_2$  10~50份  
 $\text{NaCl}$ 或 $\text{CaCl}_2$  0~5份  
 $\text{Na}_2\text{SiO}_3$  0~10份

- (2) 工艺条件：放置温度 室温~100℃  
放置时间 7天~1天

配方中 $\text{NaCl}$ 、 $\text{CaCl}_2$ 、 $\text{Na}_2\text{SiO}_3$ 均为激发剂，激发剂是为加快反应速度而拌入的激发火山灰质材料活性的物质，并非水泥促凝剂的必备成份。而 $\text{CaO}$ 或 $\text{Ca(OH)}_2$ 是必备成份，其掺量多少与放置时间和温度相关，当其它条件一定时， $\text{CaO}$ 或 $\text{Ca(OH)}_2$ 掺量愈多、放置时间越长，便可生成更多的水化产物，其促凝效果就越大。另则，放置温度越高、放置时间相对短。 $\text{CaO}$ 或 $\text{Ca(OH)}_2$ 实际掺入量可根据实际生产情况而定。是否加入激发剂也应视实际生产情况而定，加激发剂且放置温度高，可加速水化产物的生成，放置时间就相对短；不加激发剂且放置温度较低时，水化产物生成速度缓慢些，放置时间就相对长些。

本法制备的水泥促凝剂直接应用于水泥生产或施工时的水泥中，按水泥100重量份为基准计，用水泥促凝剂为2~15重量份，取代水泥或水泥混合材；掺量越多、水泥凝结越快、凝结时间越短。

采用氟硅矿化剂烧制水泥缓凝的原因是：当掺氟硅矿化剂后，由于氟的作用， $\text{Al}_2\text{O}_3$ 大量固溶入A矿及铁相中去，使熟料中C,A大量减少，这时水泥的早期凝结就只能依赖于A矿的早期水化性能。与纯C,S或不含氟的A矿相比，含氟硅A矿水化活性中心数量增多，早期水化迅速，导致了初始水化时液相中形成 $[\text{Ca}^{2+}]$ 、 $[\text{OH}^-]$ 、 $[\text{SiO}_4^{4-}]$ 、 $[\text{AlO}_4^{5-}]$ 过饱和状态和高碱度的溶液，过饱和度较大，液相为水化硅酸钙、水化铝酸钙和氢氧化钙的溶胶体，并因A矿的内吸作用，A矿表面形成了部分凝胶膜，阻碍了A矿早期的进一步水化。此外，在这种高碱度的过饱和液相中，水化硅酸钙、水化铝酸钙和氢氧化钙要经过一个较长的成核时间，且在这种条件下易形成微晶化的产物，从而导致了诱导期延长，凝结时间变慢。在一定范围内，氟掺量增加，A矿中 $\text{Al}_2\text{O}_3$ 固溶量增加，A矿水化活性越高，诱导期越长，凝结越慢。

本发明针对综上所述的实质即水化硅酸钙、水化铝酸钙和氢氧化钙成核过程的延长及晶体细化，以火山灰质材料加入一定量的 $\text{Ca(OH)}_2$ ，拌水后在一定温度下放置

一段时间，使其水化，生成一定量的水化产物：水化硅酸钙、水化铝酸钙、氢氧化钙，这就生成了水泥促凝剂所要求的主要晶种矿物，将适量的促凝剂加入到缓凝的水泥中，这些晶种作为结晶中心，能够显著加速缓凝水泥水化、促使水化硅酸钙、水化铝酸钙和氢氧化钙的析晶，使含氟硫的A矿诱导期明显缩短，从而使水泥的凝结时间大大加快。

根据上述原理，水泥熟料或水泥粉与水拌和后经放置处理也能生成作水泥促凝剂用的水化产物晶种。

本发明与背景技术相比，具有如下优点：

1、采用本法制备的水泥促凝剂可使水泥凝结时间缩短40分钟以上，取代水泥总重量的2~15%强度基本不降低。以广州石井水泥厂和高明沧江水泥厂采用氟硫矿化剂烧制的425R普通硅酸盐水泥与按本法掺入适量促凝剂后的水泥作对比，有关凝结时间和强度的对比数据见表1、表2。

2、采用本法制备水泥促凝剂的工艺条件简单，设备投资少，原料来源丰富且价廉，作为水泥混合材一次性直接掺入，可大大降低水泥生产成本，提高产质量。

3、本法从探讨机理出发，从根本上彻底解决水泥缓凝的技术难题，而且能最大限度地发挥掺氟硫矿化剂的作用，从而使氟硫矿化剂技术的应用得到进一步完善。

4、本法制备的水泥促凝剂的适用范围广，可在不改变原水泥厂现有的配料和煅烧制度，把火山灰质水泥促凝剂应用到立窑、回转窑及窑外分解窑生产的水泥中。包括因解决不了水泥缓凝问题而不敢采用氟硫矿化剂煅烧技术来降低能耗的回转窑厂，应用本发明后，亦可以放心使用氟硫矿化剂煅烧技术。具体凝结时间和强度的对比数据见表3。

实施例一：

首先以100重量份烧粘土或凝灰岩或烧页岩加入20重量份 $\text{Ca}(\text{OH})_2$ 和1.78重量份 $\text{CaCl}_2$ ，加水拌合后在55℃下放置3天，湿磨后120℃烘干，制得促凝剂A。然后掺加促凝剂A5%到高明沧江厂425R普通硅酸盐水泥中，初凝时间由4小时5分缩短至2小时36分，提前1小时29分，终凝时间由5小时15分缩短至3小时38分，提前1小时38分；3天、28天抗折、抗压强度不降低。具体数据见表2。

实施例二：

首先以100重量份粉煤灰或烧煤矸石或油页岩渣加入20重量份 $\text{CaO}$ 和3.91重量份 $\text{Na}_2\text{SiO}_3$ ，加水拌合后在室温下放置7天，湿磨后150℃烘干，制得促凝剂B。

然后掺加促凝剂B 10%到广东仁化厂霞山牌425R普通硅酸盐水泥中,初凝时间由3小时58分缩短至2小时27分,提前1小时31分,终凝时间由5小时5分缩短至4小时1分,提前1小时4分;3天、28天抗折、抗压强度降低很少。具体数据见表3。

### 实施例三:

首先以100重量份沸騰炉渣或矿渣加入16.7重量份 $\text{Ca(OH)}_2$ ,不加激发剂,加水拌合后在90℃下放置36小时,湿磨后120℃烘干,制得促凝剂C。然后掺加促凝剂C 15%到广州石井厂425R矿渣水泥中,初凝时间由3小时21分缩短至2小时9分,提前1小时12分,终凝时间由4小时24分缩短至3小时6分,提前1小时18分;3天、28天抗折、抗压强度降低很少。具体数据见表3。

### 实施例四:

首先以100重量份水泥粉加水拌合后在室温下放置1天,湿磨后110℃烘干,制得促凝剂D。然后掺加促凝剂D 15%到广州石井厂425R矿渣水泥中,初凝时间由3小时21分缩短至2小时15分,提前1小时6分,终凝时间由4小时20分缩短至3小时33分,提前51分;3天、28天抗折、抗压强度不降低。具体数据见表3。

表1

试验方案	标准稠度 (%)	初 凝 (小时:分)	终 凝 (小时:分)	强度(MPa)			
				抗 折		抗 压	
				3d	28d	3d	28d
广州石井普 硅425R	26.25	3:58	5:12	4.7	7.5	26.4	53.7
粉煤灰促凝 剂取代5%水泥	26.60	3:17	4:19	4.7	7.4	25.4	54.3
粉煤灰促凝剂 取代10%水泥	27.20	2:52	3:38	4.5	7.1	24.7	53.2
粉煤灰促凝剂 取代15%水泥	27.85	2:28	3:16	4.1	6.8	24.0	52.4

表2

试验方案	标准稠度 (%)	初 凝 (小时:分)	终 凝 (小时:分)	强度 (MPa)			
				抗 折		抗 压	
				3d	28d	3d	28d
高明沧江普 硅425R	26.8	4:05	5:15	4.5	7.8	27.4	51.3
粉煤灰促凝剂 取代5%水泥	26.8	2:50	3:52	4.1	7.3	26.7	51.6
烧粘土促凝剂 取代5%水泥	26.6	2:36	3:38	4.4	7.6	27.0	52.3
沸腾炉渣促凝剂 取代5%水泥	26.7	2:42	3:42	4.3	7.4	26.8	51.9

表3

试验方案	标准稠度 (%)	初 凝 (小时:分)	终 凝 (小时:分)	强 度 (MPa)			
				抗 折		抗 压	
				3d	28d	3d	28d
广州石井 425R <sup>*</sup> 矿渣	25.75	3:21	4:24	4.4	7.6	26.2	54.8
已水化水泥 粉促凝剂取 代5%水泥	26.2	2:15	3:33	4.3	7.8	25.9	55.2
沸腾炉渣促凝剂 取代15% 水泥	27.4	2:09	3:06	4.5	7.0	25.3	52.9
仁化霞山 425R <sup>*</sup> 普硅	25.40	3:58	5:05	5.8	8.1	28.0	51.1
粉煤灰促凝剂 取代10%水泥	27.20	2:27	4:01	4.9	7.3	27.1	50.0
珠江粤秀525# 硅酸盐 <sup>*</sup>	23.8	1:35	2:24	6.4	9.0	38.4	57.2
粉煤灰促凝剂 取代5%水泥 <sup>*</sup>	25.4	1:08	2:00	5.6	8.3	36.8	57.1

注: <sup>\*</sup>水灰比  $w/c=0.48$

## **Abstract**

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### **Method for preparing cement coagulant aid and use of the same**

A method for preparing cement coagulant aid is provided. All substances having pozzolanic activity can be used as basic materials for preparation of cement coagulant aid. Based on 100 weight parts of basic materials, 10~50 weight parts of  $\text{CaO}$  or  $\text{Ca(OH)}_2$  are added and mixed with water. The mixture is then rested to yield hydrate crystal seed such as hydrated calcium silicate and hydrated calcium aluminate. Such hydrate crystal seed also can be generated by mixing cement clinker or cement powder with water and then resting the mixture. The hydrate crystal seed is used as cement coagulant aid or to directly replace the cement admixture material. The present invention fundamentally solves the technical difficulties of slow coagulation of cement and can make use of the effect of mineralizer incorporating fluorine and sulfur maximumly, thereby, the quality of cement of shaft kiln is improved and the production cost is reduced.



## What is claimed is

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1. A method for preparing cement coagulant aid, characterized in that grinded pozzolanic material is mixed with calcium hydroxide or calcium oxide and water, the mixture is then rested to yield hydrate crystal seed such as hydrated calcium silicate and hydrated calcium aluminate etc., used as cement coagulant aid; wherein, all substances having pozzolanic activity can be used as basic materials for preparation of cement coagulant aid; based on 100 weight parts of the basic materials, the cement coagulant aid is prepared as following formulation and technical conditions:

a. Formulation:      $\text{CaO}$  or  $\text{Ca}(\text{OH})_2$      10 ~50 parts

$\text{NaCl}$  or  $\text{CaCl}_2$              0 ~ 5 parts

$\text{Na}_2\text{SiO}_3$                  0 ~ 10 parts

b. Technical conditions: Resting temperature: room temperature ~ 100°C

Resting time: 7 days ~ 1 day

2. A method for preparing cement coagulant aid, characterized in that cement clinker or cement powder is mixed with water, the mixture then is rested to yield hydrate crystal seed used as cement coagulant aid.

3. A method for preparing cement coagulant aid according to claim 1, characterized in that the pozzolanic material include burned clay, burned shale, flyash, oil shale feculence, burned coal gangue, tuff, boiling slag, mineral feculence or pozzolan.

4. A use of cement coagulant aid, characterized in that 2~15 weight parts of cement are replaced by the cement coagulant aid produced by the method of claim 1, 2 or 3 based on 100 weight parts of basic materials, for speeding up cement coagulation.

5. A use of cement coagulant aid according to claim 4, characterized in that said cement coagulant aid can directly replace the cement admixture material.

### **Method for preparing cement coagulant aid and use of the same**

The present invention relates to industrial technology of cement production and, more particularly, to a method for preparing cement coagulant aid and a use of the same.

Ever since 1950s, the technology of using calcium fluoride as the mineralizer to produce cement has being applied abroad. This technology can improve the burnability of raw material of cement, accelerate the generation of mineral A (alite) and increase its hydrated activity. Therefore, it has become one of the most effective ways for the shaft kiln cement plants to improve the production and quality and reduce the consumption. Ever since the beginning of 1980s, technology of complex mineralizer incorporating fluorine and sulfur has been widely applied in the shaft kiln cement factories in China and biggish economic benefits have been obtained. However, when cement is produced with complex mineralizer incorporating fluorine and sulfur, large amount of  $Al_2O_3$  solid-solve into mineral A or iron phase under the action of fluorine, which make  $C_3A$  in the clinker decrease greatly and the induction period of hydration of alite to be prolonged. As a result, the coagulation time of cement is often prolonged. In the actual application, the construction speed and engineering quality are influenced due to slow coagulation of cement.

In order to solve the problem of slow cement coagulation, most of plants have to reduce the quantity of calcium fluoride in cement. However, the insufficient quantity of calcium fluoride incorporated into cement will not only weaken the effect of mineralizer, but also reduce the activity of mineral A. As a result, the cement strength decrease tremendously. On pages 7-12 of issue 4 in 1994 of *Cement*, an article titled "Analysis on Reasons of Slow Coagulation of Clinker and its Preventative Measures in Zhenjiang Cement Company", described the measures for improving the slow coagulation of cement clinker containing fluorine and sulfur from the aspects of formulation and calcination as follows: control  $F/SO_3$  within 0.42~0.55, create conditions for incorporating aluminum corrective material, incorporate 5% purchased early strength of clinker when the clinker is being ground into powder, then adopt the system of calcinating rapidly and cooling urgently, so that the initial coagulation time of clinker could be controlled within 3.5 hours. But it had its disadvantages. First, it changed the original production technology and

conditions and requires stable formulation and calcination. Second, the cost is too expensive for early strength clinker used as the additive.

It is still a big technical difficulty for the cement plants to make use of the effect of mineralizer containing fluorine and sulfur maximumly while to control the cement coagulation time well.

The purpose of the present invention is to overcome the shortages of background art, that is, to develop a cement coagulant aid, which can not only make use of the effect of mineralizer containing fluorine and sulfur maximumly, but also can control the cement coagulation time well. When the cement is being produced or used, addition of proper amount of cement coagulant aid can not only fundamentally solve the technical difficulty of slow cement coagulation, which further perfect the technology of fluorine-sulfur mineralizer, but also improve the quality of cement of shaft kiln, with the production cost being reduced. Meanwhile, there is no any negative effect be brought to cement performances.

The purpose of the present invention can be realized by the following measures:

Starting from study of the mechanism of slow coagulation of cement calcinated with mineralizer containing fluorine and sulfur and through a great deal of experiments and analysis, the present invention has found out substances having pozzolanic activity to be used as basic materials for the coagulant aid. These substances include burned clay, burned shale, flyash, oil shale feculence, burned coal gangue, tuff, boiled slag, mineral feculence or pozzolan. In a word, all substances which can be mixed with calcium hydroxide or calcium oxide and water and then rested to generate hydrate product such as hydrated calcium silicon and hydrated calcium aluminate etc., can be used as the basic materials for preparation of cement coagulant aid.

Based on 100 weight parts of the basic materials, the cement coagulant aid is prepared as following formulation and technical conditions:

- a. Formulation:      $\text{CaO}$  or  $\text{Ca}(\text{OH})_2$      10 ~50 parts  
                              $\text{NaCl}$  or  $\text{CaCl}_2$              0 ~ 5 parts

$\text{Na}_2\text{SiO}_3$

0 ~ 10 parts

b. Technical conditions: Resting temperature: room temperature ~ 100°C

Resting time: 7 days ~ 1 day

In this formulation,  $\text{NaCl}$ ,  $\text{CaCl}_2$  and  $\text{Na}_2\text{SiO}_3$  are all stimulus. The stimulus is the substance incorporated for stimulating the activity of pozzolanic material, thereby accelerating the reaction speed, rather than an essential ingredient of cement coagulant aid. However,  $\text{CaO}$  or  $\text{Ca}(\text{OH})_2$  is an essential ingredient and its quantity is related with resting time and temperature. While other conditions remain constant, the bigger the quantity of  $\text{CaO}$  or  $\text{Ca}(\text{OH})_2$  incorporated is and the longer the resting time is, the more hydrates are generated and the better coagulation effect is. Besides, the higher the resting temperature is, the shorter the resting time is. However, the actual incorporating quantity of  $\text{CaO}$  or  $\text{Ca}(\text{OH})_2$  can be determined in accordance with the actual production conditions. Whether or not to add stimulus is also determined in accordance with the actual production conditions. Addition of stimulus and higher resting temperature may accelerate the generation of hydrate product and shorten the resting time. When no stimulus is added and the resting temperature is comparatively shorter, the generation speed of hydrate product will be slower and the resting time will be relatively longer.

The cement coagulant aid prepared by this method is directly used in the cement in cement production or construction. Based on 100 weight parts of cement, 2~15 weight parts of cement coagulant aid are used to replace cement or the cement admixture material. The bigger the incorporated quantity is, the rapider the cement coagulates, and the shorter the coagulation period is.

The reasons for slow coagulation of cement produced from mineralizer containing fluorine-sulfur are as follows: when the fluorine-sulfur mineralizer is incorporated, a large amount of  $\text{Al}_2\text{O}_3$  solid-solved into mineral A and the iron phase due to the action of fluorine, which make  $\text{C}_3\text{A}$  in the clinker reduce greatly. At this time, the early coagulation of cement has to only depend upon the early hydration performances of mineral A. Compared with the pure  $\text{C}_3\text{S}$  or mineral A without fluorine, the quantity of hydrated activity centers of mineral A containing fluorine and sulfur increases and the early hydration is rapid, resulting in generation of liquid

with over-saturated state of  $[Ca^{++}]$ ,  $[OH^-]$ ,  $[SiO_4^{4-}]$  and  $[AlO_4^{5-}]$  and the high-alkaline degree in the liquid phase during stage of primary hydration. In this case, the degree of oversaturation is bigger, the liquid is a sol of hydrated calcium silicon, hydrated calcium aluminate and calcium hydroxide. Besides, due to the internal absorption of mineral A, gel film is formed on part of surface of mineral A, which prevent early further hydration of mineral A. Additionally, in the oversaturated liquid phase of high-alkaline degree, a long period of time is needed for the nucleation of hydrated calcium silicon, hydrated calcium aluminate and calcium hydroxide. Moreover, under this condition, the micro-crystallized product is easy to be generated, resulting in the prolonged induction period and slow coagulation. In a certain range, the increase of quantity of fluorine incorporated may bring about the increase of  $Al_2O_3$  solid-solution quantity in mineral A. The higher hydrated activity of mineral A is, the longer induction period and the slower coagulation are.

To be aimed at the above-mentioned fact that the nucleation process of hydrated calcium silicon, hydrated calcium aluminate and calcium hydroxide are extended and the crystals are thinned, the present invention uses pozzolanic material as basic materials to which a certain quantity of  $Ca(OH)_2$  are added and mixed with water, the mixture is then rested under a certain temperature for a certain period of time to be hydrated, thereby yielding a certain quantity of hydrate products: hydrated calcium silicon, hydrated calcium aluminate and calcium hydroxide, that is, yielding main crystal seed minerals required by cement coagulant aid. When a proper amount of coagulant aids are added to the cement which coagulates slowly, these crystal seed, as the crystallization center, are able to tremendously accelerate the hydration of cement which coagulates slowly and boost the crystallization of hydrated calcium silicon, hydrated calcium aluminate and calcium hydroxide. Resultantly, the induction period of mineral A containing fluorine and sulfur could be obviously shortened, thereby accelerating the coagulation speed of the cement.

Based on the above-mentioned principles, such hydrate crystal seed used as cement coagulant aid also can be generated by mixing cement clinker or cement powder with water and then resting the mixture.

Compared with the background art, the present invention has following advantages:

1. The cement coagulant aid prepared by this method can shorten the cement

coagulation time by more than 40 minutes, while the strength is basically not reduced when 2~15% of the total weight of cements are replaced. The cement produced by incorporating proper quantity of coagulant aids in accordance with this method is compared with 425R ordinary silicate cement of Guangzhou Shijing Cement Company and Gaoming Cangjiang Cement Company produced using fluorine-sulfur mineralizer, the comparison datas of coagulation time and strength are shown in tables 1 and 2.

2. Due to adoption of this method for preparation of cement coagulant aid, technological condition is simple, investment on equipment is small, raw material is abundant and cheap. The coagulant aid can be incorporated directly at one time as the cement admixture material, which can greatly reduce the production cost of cement and improve the quantity and quality.

3. Starting from the research on the mechanism, this method fundamentally solves the technical difficulties of slow coagulation of cement and can make use of the effect of mineralizer incorporating fluorine and sulfur maximumly, thereby, further improve the application of technology of mineralizer incorporating fluorine and sulfur.

4. The cement coagulation prepared by this method has a wide application range. The pozzolan cement coagulant aid can be used to the cement produced in shaft kiln, rotary kiln and dissolution kiln without changing original system of formulation and calcination in cement plants. After adopting the invention, even those rotary kilns which dare not to adopt the fluorine-sulfur mineralizer technology to reduce the energy consumption being afraid that they can not solve the cement coagulation problem, also can use the calcinations technology using fluorine-sulfur mineralizer at ease. The comparison datas for the specified coagulation time and strength are shown in table 3.

### **Example 1**

First, to 100 weight parts of burned clay or tuff or burned shale, 20 weight parts of  $\text{Ca}(\text{OH})_2$  and 1.78 weight parts of  $\text{CaCl}_2$  were added. Water was then added and mixed evenly. The mixture was remained for 3 days under a temperature of  $55^\circ\text{C}$ . After being grinded wetly, the mixture was then dried under a temperature of  $120^\circ\text{C}$

to obtain coagulant aid A. 5% coagulator A was then incorporated to 425R ordinary silicate cement of Gaoming Cangjiang Cement Company. As a result, the initial coagulation time was reduced from 4 hours and 5 minutes to 2 hours and 36 minutes, with an advance of 1 hour and 29 minutes. The final coagulation time was reduced from 5 hours and 15 minutes to 3 hours and 38 minutes, with an advance of 1 hour and 38 minutes. The strength of fold resistance and the pressure resistance after 3 days and 28 days did not decrease. The specified datas were shown in table 2.

### **Example 2**

First, to 100 weight parts of flyash or burned coal gangue or oil shale feculence, 20 weight parts of CaO and 3.91 weight parts of  $\text{Na}_2\text{SiO}_3$  were added. Water was then added and mixed evenly. The mixture was remained for 7 days under room temperature. After being grinded wetly, the mixture was then dried under a temperature of  $150^\circ\text{C}$  to obtain coagulant aid B. 10% coagulator B was then incorporated to Xiashan 425R ordinary silicate cement of Guangdong Renhua Company. As a result, the initial coagulation time was reduced from 3 hours and 58 minutes to 2 hours and 27 minutes, with a advance of 1 hour and 31 minutes. The final coagulation time was also reduced from 5 hours and 5 minutes to 4 hours and 1 minute, with a advance of 1 hour and 4 minutes. The strength of fold resistance and the pressure resistance after 3 days and 28 days did not decrease. The specified datas were shown in table 3.

### **Example 3:**

First, First, to 100 weight parts of boiled slag or mineral feculence, 16.7 weight parts of  $\text{Ca}(\text{OH})_2$  and no stimulus were added. Water was then added and mixed evenly. The mixture was remained for 36 hours under a temperature  $90^\circ\text{C}$ . After being grinded wetly, the mixture was then dried under a temperature of  $120^\circ\text{C}$  to obtain coagulant aid C. 15% coagulator C was then incorporated to 425R mineral feculence cement of Guangdong Shijing Company. As a result, the initial coagulation time was reduced from 3 hours and 21 minutes to 2 hours and 9 minutes, with a advance of 1 hour and 12 minutes. The final coagulation time was also reduced from 4 hours and 24 minutes to 3 hours and 6 minutes, with a advance of 1 hour and 18 minutes. The strength of fold resistance and the pressure resistance after 3 days and 28 days did not decrease. The specified datas were shown in table 3.

**Example 4:**

First, to 100 weight parts of cement powder, water was added and mixed evenly. The mixture was then remained for 1 days under room temperature. After being grinded wetly, the mixture was then dried under a temperature of 110°C to obtain coagulant aid D. 15% coagulator D was then incorporated into 425R mineral feculence cement of Guangdong Shijing Company. As a result, the initial coagulation time was reduced from 3 hours and 21 minutes to 2 hours and 15 minutes, with a advance of 1 hour and 6 minutes. The final coagulation time was also reduced from 4 hours and 20 minutes to 3 hours and 33 minutes, with a advance of 51 minutes. The strength of fold resistance and the pressure resistance after 3 days and 28 days did not decrease. The specified datas were shown in table 3.

**Table 1**

Test scheme	Standard consistency (%)	Initial coagulation time (h: m)	Final coagulation time (h: m)	Strength (Mpa)			
				Fold resistance		Pressure resistance	
				3d	28d	3d	28d
Ordinary silicate cement 425R of Guangzhou Shijing	26.25	3:58	5:12	4.7	7.5	26.4	53.7
Flyash coagulant aid instead of 5% cement	26.60	3:17	4:19	4.7	7.4	25.4	54.3
Flyash coagulant aid instead of 10% cement	27.20	2:52	3:38	4.5	7.1	24.7	53.2
Flyash coagulant aid instead of 15% cement	27.85	2;28	3:16	4.1	6.8	24.0	52.4



**Table 2**

Test scheme	Standard consistency  (%)	Initial coagulation time  (h.m.)	Final coagulation time  (h.m.)	Strength (Mpa)			
				Fold resistance		Pressure resistance	
				3d	28d	3d	28d
Ordinary silicate cement 425R of Gaoming Cangjiag	26.8	4:05	5:15	4.5	7.8	27.4	51.3
Flyash coagulant aid instead of 5% cement	26.8	2:50	3:52	4.1	7.3	26.7	51.6
Burned clay coagulant aid instead of 5% cement	26.6	2:36	3:38	4.4	7.6	27.0	52.3
Boiling slag coagulant aid instead of 5% cement	26.7	2:42	3:42	4.3	7.4	26.8	51.9

**Table 3**

Test scheme	Standard consistency (%)	Initial coagulation time (h: m)	Final coagulation time (h: m)	Strength (Mpa)			
				Fold resistance		Pressure resistance	
				3d	28d	3d	28d
425R* slag cement of Guangzhou Shijing	25.75	3:21	4:24	4.4	7.6	26.2	54.8
Hydrated cement powder coagulant aid instead of 5% cement	26.2	2:15	3:33	4.3	7.8	25.9	55.2
Boiling slag coagulant aid instead of 15% cement	27.4	2:09	3:06	4.5	7.0	25.3	52.9
Xiashan ordinary cement 425R of Renhua	25.40	3:58	5:05	5.8	8.1	28.0	51.1
Flyash coagulant aid instead of 10% cement	27.20	2:27	4:01	4.9	7.3	27.1	50.0
Yuexiu 525# silicate cement of Zhujiang	23.8	1:35	2:24	6.4	9.0	38.4	57.2
Flyash coagulant aid instead of 5% cement	25.4	1:08	2:00	5.6	8.3	36.8	57.1

Note: \* water/cement ratio  $w/c = 0.48$